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BOND FISSION. POSSIBLE MECHANISM FOR THE PROCESS

by

Philip J. Elving, Joseph M. Markowitz and Isodore Rosenthal

Technical Report No. 2

to the

OFFICE OF NAVAL RESEARCH  
Under Project No. NR 051-318  
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at the  
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EFFECT OF CHAIN BRANCHING ON ELECTROCHEMICAL CARBON-HALOGEN  
BOND FISSION. POSSIBLE MECHANISM FOR THE PROCESS<sup>1</sup>

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<sup>1</sup>No. XVI in a series of papers on the polarographic behavior of organic compounds.

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ABSTRACT

In order to establish a better basis for correlating chemical reactivity with polarographic behavior of carbon-halogen bonds, an attempt has been made to ascertain whether the electrochemical process involves an elimination or free radical mechanism. The present study presents evidence derivable from structural influences.

A group of branched chain alpha-bromoalkanoic acids with several of their ethyl esters and straight chain isomers were investigated polarographically. The relation between half-wave potential,  $E_{1/2}$ , and pH for the acids follows an S-shaped pattern having pH-invariant regions in the alkaline and acidic ranges,  $E_{1/2}$  in the latter region being considerably more negative. The  $E_{1/2}$  values for the esters are pH-independent, being slightly more positive than those of the corresponding acids in the acidic region. The polarographic waves all involve a two-electron reduction process, and are all diffusion-controlled. In the acidic region, the branched chain acids are more easily reducible than their straight chain isomers by 0.20 to 0.13 v., the larger differences being observed for the lower molecular weight acids. In the alkaline region the situation is similar, but there are some apparent anomalies.

The possible course of the electrode reaction is considered in the light of the influence of pH, of chain length and of chain branching. Certain aspects of a possible analysis of the pH-dependence are discussed and shortcomings of previous theoretical treatments are noted. Tentative hypotheses for a plausible reaction mechanism are advanced in terms of contemporary organic reactivity theory and steric concepts. Evidence is examined for an elimination process of either  $S_N1$  or  $S_N2$  pattern for the carbon-halogen bond fission, and some consideration is given to the possibility of a free radical mechanism. The anomalous behavior in the alkaline region is explained as the result of formation of certain ring-structures which can achieve stability only in the acids which behave anomalously.

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#### INTRODUCTION

Previous polarographic work on electrochemical carbon-halogen bond fission in alpha halogenated alkanic acids is reviewed in a study (1) of the straight chain acids. At all pH values, as chain length increases, observed  $E_1$  decreases, there being one exception, bromobutyric, in the alkaline pH region. The bond-fission involves a two-electron reduction with conversion to the corresponding saturated acid. The effect of ethanol on  $E_1$  and on diffusion current,  $i_d$ , is also discussed, as are the influences of structure and inductive effect on the ease of reduction.

It seemed logical to inquire next into the effect of branching of the carbon chain and of increasing subsequent chain lengths on the ease of reduction. Consequently, bromoacetic acid (HH), 2-bromopropionic acid (HH), 2-bromobutyric acid (EH), 2-bromo-2-methylpropionic acid (MH), 2-bromo-2-methylbutyric acid (ME), 2-bromo-2-ethylbutyric acid (EE) and 2-bromo-2-ethylhexoic acid (BE) were studied, the first three for

comparison with the previous study (1)<sup>1</sup>. In order to complete the work,

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<sup>1</sup>For brevity and clarity, the various acids will be subsequently referred to through the use of the abbreviations indicated. These consist of the initial letters of the substituents, other than bromine, on the alpha carbon atom, i.e., H is hydrogen, M is methyl, E is ethyl, etc.; In the case of the ethyl esters, Et will be prefixed, e.g., EtMH is ethyl-2-bromopropionate.

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the ethyl esters of five of these acids were investigated.

One of the objectives of the systematic study of the electrochemical fission of carbon-halogen bonds being carried on by the senior author and his coworkers is the definition of a possible basis for correlating organic chemical reactivity of these bonds with the polarographically defined half-wave potentials. Since both the chemical and electrochemical processes are usually irreversible in nature, comparison such as indicated would be valid only if both processes involved the same essential reaction pattern. For this reason, an attempt is being made to ascertain whether the electrochemical process is an elimination reaction of the  $S_N1$  or  $S_N2$  type, or a free radical process.

The observed behavior of the acids and esters in the present study is considered from several points of view, e.g., the prediction of ease of bond fission from the principle of permanent polarization, and the compatibility of observed behavior on substitution with that predicted for different elimination mechanisms.

Another matter requiring extensive consideration is the consistently observed and repeatedly verified result (1-6) that for  $\alpha$ -haloalkanoic acids,  $E_1$  varies with pH in an S-shaped pattern. This behavior has never been satisfactorily explained on a quantitative basis, although related phenomena in other groups of compounds, e.g., the double wave in pyruvic acid, have been successfully treated (7,8). It is not clear at present whether the S-shaped curve requires merely a modification of some of

these treatments or whether entirely new concepts are required. An attempt by Saito (9) to use a modification of Brdicka and Wiesner's (7) approach to the problem is quite unsatisfactory. An attempt is being made to formulate a consistent treatment of this matter, and its discussion will be the subject of forthcoming work. Accordingly, the phenomenon of the S-shaped curve is given only brief attention in the present paper.

#### EXPERIMENTAL

The experimental conditions differ somewhat from those of previous work (1, 2, 3). The following buffer systems, adjusted to an ionic strength of 0.5 M, were used: HCl-KCl (pH 1 to 2),  $\text{HC}_2\text{H}_3\text{O}_2\text{-NaC}_2\text{H}_3\text{O}_2$  (pH 4 to 6), and  $\text{NH}_3\text{-NH}_4\text{Cl}$  (pH 8 to 9). The operating temperature was 0°; the test solution contained 9.5% ethanol by volume; the mercury head was 50 cm. Supplementary measurements were made at 25°, and others at 75 cm. The capillary used was Corning marine barometer tubing, having a drop-time of 5.94 sec. and an  $m$ -value of 1.071 mg./sec. at open circuit in distilled water (50 cm., 0°). Temperature control to  $\pm 0.1$  degree was achieved by using a specially constructed polarographic H-cell immersed in an ice bath. A Sargent Model XXI Polarograph was used in connection with a Leeds and Northrup student-type potentiometer. All potentials given are corrected for IR drops and are referred to the S.C.E. Beckman Model G and H pH meters <sup>were</sup> used to measure pH. In view of the 9.5% ethanol content of the test solutions, strict interpretation of the pH values is unwarranted; accordingly, pH values are given to only one decimal place in the summary table (Table VII) even though measured to  $\pm 0.02$  pH units and so reported in the primary data tables (Tables I to VI).

MM, EE, EtBe, EtEE and EtMM were obtained from Sapon Laboratories. EtEH, EtMH, HH, MH, and EH were Eastman Kodak white label grade chemicals. ME and BE were synthesized. No special attempt was made to purify these

compounds except for ME and BE which were, of course, purified in the course of their synthesis. The former distilled at 104-107°/8 mm. and the latter at 100-101°/2 mm. All compounds were found to be polarographically pure.

Test solutions were prepared by diluting a 5-ml. portion of stock solution, containing a known concentration of the compound in 95% ethanol, to 50 ml. with buffer solution. All stock solutions were prepared at 0°; stock and buffer solutions were stored at 0°. Concentration and pH values subsequently given are those of the final test solutions. Solutions were deoxygenated with nitrogen, purified as described (2). Base solution (obtained by mixing 95% ethanol with buffer) curves were used in every case to correct the test solution curves.

Choice of operating conditions was governed by the following factors; the poor solubility of some of the compounds in water indicated the necessity for a mixed solvent; the use of ethanol and the proportion of 9.5% by volume were somewhat arbitrary, being selected on the basis of solubility improvement and minimum  $E_3$  effect. At 25° the rapid hydrolysis of some compounds, particularly in alkaline media, even during the relatively short period of deoxygenation and electrolysis, resulted in curves worthless for calculation; the disturbance was effectively eliminated at 0°.

#### OBSERVED BEHAVIOR

All the acids exhibited a sigmoidal variation of  $E_3$  with pH, the curve having flat portions in the acid region below pH 2 and in the alkaline region above pH 8; values of  $E_3$  in these invariant regions are given in Table VII and are plotted in Fig. 1 against the number of carbon atoms. Complete data for the acids are given in Tables I to IV and VI. Fig. 1 includes a similar plot for the straight chain 2-bromoalkanoic acids (1). Since the latter data were obtained under somewhat different

experimental conditions (temperature difference and alcohol absence), the curve is displaced along the ordinate. However, the similarity in the trends of these acids covered by both sets of data (HH, HM and EH) is such that a qualitative extrapolation may be made for purposes of comparison. This plot and its interpretation constitute the basis of much of the subsequent discussion.

In the acid pH region, the acids exhibit a continuous decrease in (negative)  $E_1$  with increasing chain length, i.e., they become more easily reducible. There is a sharp break between the straight chain acids and their branched chain isomers, the latter being more easily reducible. Following this break, the trend is almost the same for both series.

In the alkaline region, the situation is more complicated. In general, there is again a continuous decrease of  $E_1$  with increasing molecular weight in both series of acids, there being, however, three anomalies: EH in the straight chain series, and ME and KE in the branched series. The increment in  $E_1$  between respective non-anomalous members of both series is greater than the corresponding increment in the acid region. It is significant, as subsequently shown, that all three anomalies are encountered in molecules with one or two ethyl substituents on the alpha carbon atom.

Because of the anomalous behavior of ME and KE in the alkaline region, there is a cross-over in the plots of the branched and straight series. However, the trend of the curves seems to be in the direction of a reversal of this cross-over, perhaps at the  $C_9$  level.

Temperature coefficients of  $i_d$  and current ratios upon variation of the mercury head agree closely with the theoretical values consequent to diffusion-controlled current-producing processes. The  $\alpha$  values, the empirical constants in the equation for  $E_1$  (10), vary from 0.6 to 0.7 in the acid region to 0.3 or 0.4 in the alkaline region. Diffusion current



constants,  $I$ , are lower in the alkaline region than in the acid region and pass through a minimum in the intermediate region.

The  $E_1$  values for the esters (Table V) are invariant with pH. Such slight variations as do occur can be attributed to the specific effect of the differing buffer systems used. Variation of ester  $E_1$  with number of carbon atoms in the parent acid is shown in Fig. 1. The ester  $E_1$  is in each case very close to  $E_1$  of the corresponding acid in the acid region, being slightly less negative. These results agree with previous observation (4, 5). The activating influence of the carbonyl group on the carbon-halogen bond fission is emphasized by the fact that the  $\beta$ -bromoalkanoic acids and esters do not show reduction within the observable potential range.

#### DISCUSSION

The principal effects to be considered are (a) the pH-dependency of  $E_1$  in the case of the acids, (b) the decrease of (negative)  $E_1$  with increase of chain length, (c) the effect of chain branching, and (d) the apparent anomalies in the alkaline region with respect to decrease of (negative)  $E_1$  with chain length.

##### Dependency of $E_1$ on pH

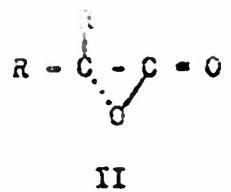
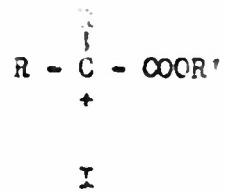
Although a detailed analysis of the sigmoid relation between  $E_1$  and pH cannot now be presented, certain aspects of the phenomena involved will be discussed.

Only one polarographic wave appears in the fission of the carbon-halogen bond in  $\alpha$ -halo acids and esters; this wave is diffusion-controlled. We can thus be fairly certain that the kinetic process of acid-anion equilibration is not directly rate-controlling. Consequently, one or another of the following processes probably prevails: (a) Only one of the equilibrium forms is reducible over the potential span used; its  $E_1$  is pH-dependent. (b) Both forms are reducible and the form reducible

at the less negative potential is reduced preferentially over the whole pH range; its  $E_1$  is pH-dependent. (c) Both forms are reducible and one or both of the forms have  $E_1$  pH-dependent; the separate curves of  $E_1$  vs. pH cross, i.e., one form is preferentially reduced over one end of the pH range, and the other form over the other end. (d) Both forms are reducible with pH-independent  $E_1$ ; the rising portion of the curve is due to some as yet undetermined feature of the electrode process kinetics.

One question which can fairly be answered at this stage is the nature of the more readily reducible form, which has been assumed in previous work to be the undissociated acid, a conclusion which is highly probable. In the first place, Brdicka and Wiesner (7) made this assumption in the case of pyruvic acid; their mathematical treatment produced calculated results in good agreement with the data. Secondly, the ethyl esters of the haloacids, which are more closely related to the undissociated acid form than to the anion of the parent acid, have pH-invariant  $E_1$  values very close to those of the acids in the acid region (Fig. 1, Table V; references 4, 5). It is also important in this connection to emphasize that the data on the esters indicate that the fundamental phenomenon of carbon-halogen bond fission is itself pH-independent; thus, the pH-dependence of  $E_1$  for the acids must be ascribed to other phenomena.

An interpretation of the greater ease of reduction of the ester or acid compared to the anion can be given on the basis of electronic polarization, if the  $S_N1$  mechanism is assumed. In the anion, such a mechanism would produce at the electrode on fission of the carbon-halogen bond a transitory species with a local positive charge on the alpha carbon atom and a local negative charge on the terminal oxygen atoms. Internal compensation might then lead to a stabilized alpha-lactone structure (II) (11-13) much less labile than the corresponding undissociated acid or ester intermediate (I):



R and R' refer either to hydrogen or to alkyl groups.

There are several possible assumptions about the nature of the pH-dependency, which may be divided into two groups: (a) Those in which hydrogen ion activity enters as a factor in the mass action effect for acid dissociation, as involved either in the kinetics of the equilibration or in reducing the number of mathematical variables by substitution. (b) Those in which hydrogen ion enters because of its role in the gross electrode process itself. Results of the assumptions in (a) applied to the present case are semi-empirical and make generally poor fits with the data. On the other hand, the assumptions consequent to (b) have never been adequately discussed. For instance, the electroreduction is coupled, kinetically, with the diffusional process. In the classical analysis, this coupling is treated only from the point of view of diffusion, i.e., only when the potential has reached a value at which the rate of diffusion is the limiting process (10). But at the  $E_{\frac{1}{2}}$  value, this point has not been reached, i.e., the electroreduction is still the process which is rate-controlling. Yet the lack of applicability of the Ilkovic equation at potentials less than those corresponding to the limiting portion of the wave is never seriously questioned, e.g., it is conventionally (and conveniently) assumed that when  $E = E_{\frac{1}{2}}$ , the surface concentration is equal to one-half the bulk concentration, and so on for other points on the wave, although the boundary condition for the solution of the differential equation for diffusion to a growing spherical surface is, to quote Kolthoff and Lingane (10),

$$C_s \ll C_b \text{ or } C_s = 0 \text{ when } t > 0$$

It is the authors' view that treatment of these and other inconsistencies in basic polarographic theory must be undertaken before final answers to questions like the pH-dependence of polarographic waves can be found.

### Effect of Chain Length

The possible interpretation of this effect can be presented from several viewpoints. If the reaction proceeds by an  $S_N1$  mechanism, the decrease in (negative)  $E_1$  with chain length would be expected, because the electron drift from the alkyl substituents would serve to make the fractional charge on the alpha carbon progressively less positive as the number and size of the substituents increased. This would progressively weaken the carbon-bromine bond, and the dissociation of the bromine would become steadily less difficult. Consequently, the electroreduction would occur at a progressively less negative  $E_1$ . This argument is open to the possible objection that the continuation of the trend in the higher acids would violate the concept of permanent polarization. The latter holds the influence of electron-repelling groups toward a positive center to be negligible at a distance of more than one carbon atom. We would therefore expect a change in the reactivity of the alpha-carbon-bromine bond in going from bromoacetic to bromopropionic acid, and perhaps even a further change on going to bromobutyric acid; beyond this point, no further change should be expected. This expectation is contradicted by the data.

In discussing the straight chain acids, Rosenthal, Albright and Elving (1) indicate that the apparent conflict cited is due to the operation of such factors as ease of approach to, orientation to, and adsorption on the electrode surface. In particular, they consider that adsorption may be the principal factor in causing the steady decrease in  $-E_1$  with chain length. They cite work (14) on the adsorption on mercury of the normal primary alcohols from the vapor phase, in which it is shown that there is a regular increase in free energy as chain length increases. If a similar situation exists in the case of adsorption of the acids on mercury from solution, and if the adsorption is fast

enough so that it is not the rate-determining step, the electrode reaction could take place within the adsorbed film, and still reveal itself as diffusion-controlled. Thus, differences in the energy of adsorption would be the primary potential-controlling condition, rather than differences in bond strength in the acids, although the factors are related. An  $S_N1$  mechanism could still be defended in such a case; the well-known effect of the solvent in being conducive to dissociation could be assumed by the field of the mercury electrode.

The possibility of an  $S_N2$  mechanism, involving back-side approach by a nucleophilic agent, cannot be dismissed. In This case, electrons from the electrode would themselves constitute the nucleophilic agent. At first glance, such a mechanism seems to be in direct conflict with the data, because substitution of alkyl substituents, as discussed previously, would make the alpha carbon less positive, thus decreasing its attraction for a nucleophilic agent. Such a mechanism, if it were the potential-determining step, would cause an increase in  $-E_1$  with chain length. On the other hand, the effect of an increased electron drift might be compensated for by stretching of the carbon-bromine bond. In any case, if the adsorption hypothesis is correct, either  $S_N1$  or  $S_N2$  effects would be masked and no decision on the basis of present evidence is possible.

The idea of the  $S_N1$  mechanism is still attractive, however, because (a) it explains the sharp drop in  $-E_1$  going from HH to MH followed by the smaller drop from MH to EH; (b) it explains the more difficult reduction of the anion form compared to the undissociated acid; and (c) it explains the effect of branching, discussed in the next section.

It is obviously desirable to distinguish among possible mechanisms by a study of an acid such as ME with an asymmetric alpha carbon in order to ascertain whether optical activity is retained during reduction, and,

if so, whether configuration is retained. In  $S_N2$  mechanisms, there is reversal of configuration, while configuration is retained in  $S_N1$  and very rapid  $S_N1$  processes. There is loss of activity in most  $S_N1$  and free radical processes. It is planned to investigate electrochemical carbon-halogen bond fission in an optically active compound.

#### Effect of Chain Branching

Branching has a very pronounced effect on  $E_1$  (Fig. 1). In the acid region, the difference in reducibility between corresponding isomers in the straight and branched series varies from 0.20 to 0.13 v., going from the  $C_4$  to  $C_8$  isomers. The difference appears to converge gently, indicating that in the higher acids the effect of branching on reducibility would be negligible. In the alkaline region, because of the anomalous phenomena encountered, the effect of branching is not so clearly delineated, though the effect is quite evidently present.

The pronounced effect of branching in the acid region is explicable on the basis of permanent polarization. The combined effects of two alkyl substituents on the same carbon atom will be much greater than the effect of one substituent alone. There is ample evidence to support this in the known lability of tertiary carbon atoms as compared with the secondary or primary carbon atoms. In addition, there is the possibility of B-strain due to the increased substitution. Elving and Westover (15) found the polarographic behavior of the butyl bromides to be in accord with the effects observed here, although the differences were not so striking. They find  $E_1$  values of -2.47, -2.44, and -2.35 volts for *n*-butylbromide, *iso*-butylbromide and *sec*-butylbromide, respectively. An  $S_N1$  mechanism is in accord with this type of progression, since such reactions are favored by increasing complexity of substitution (16, 17).

It is noteworthy, in connection with the foregoing discussion of the dependence of  $E_1$  upon structure, that Taft (18) has been able to



correlate the  $E_1$  data for the alpha bromoalkanoic acids at pH 1.1 reported in this paper with Hammett's polar substituent sigma-values (12). The calculated rho-value for this correlation is  $0.397 \pm 0.02$ .

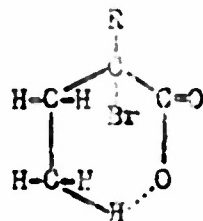
Before concluding the discussion of probable mechanisms, the possibility of free radical formation must be considered. That such reactions may occur in electrode processes is demonstrated, for example, by the work of Haggerty (19) and Wheland's treatment of it (20), in which it is shown that the reduction of acetone at a mercury cathode gives rise to both mercury diisopropyl and pinacol; this suggests the transitory existence of the isopropyl radical as well as the structure  $(\text{CH}_3)_2\dot{\text{C}}-\text{O}^-$  or  $(\text{CH}_3)_2\dot{\text{C}}-\text{OH}$ . Free radicals have also been postulated in the Kolbe synthesis, e.g., see reference 21.

The free radical mechanism postulated must be compatible not only with the stoichiometric reaction but also with the shift of  $E_1$  with chain length and with branching. The following considerations satisfy these requirements: (a) The free radical formed can acquire an electron to form a carbanion, or it may pick up a hydrogen atom to complete the gross reaction. (b) As chain length increases, the resonance energy of an alkyl free radical increases (22). Thus, if the potential-determining step is the breaking of the C-Br bond to form a free radical and if the bond strengths are nearly constant (as expected from the concept of permanent polarization), the differences in resonance energy account for the trend of the  $E_1$  values. (c) The initial effect of branching can be accounted for by the decrease in bond strength associated with tertiary substitution, while the subsequent and gentler decrease in  $-E_1$  can be justified on the same basis as in (b).

#### The Anomalies in the Alkaline Region

It is proposed that the anomalous behavior encountered in the alkaline pH region has its source in the tendency toward stable ring formation found in compounds having six-member chains with terminal atoms differing in

electronegativity. In each of the compounds exhibiting anomalous behavior, i.e., EH, ME and EE, which are reduced at substantially more negative potentials than would be expected from the trend of the neighboring acids, there is a possibility of forming at least one six-membered ring:



In the case of the only other acid among those studied where a six-membered ring could be formed, BE, the data for comparison (on the longer-chain side) are not available.

Construction of Fisher-Hirschfelder-Taylor models of the acids showing anomalous behavior tends to confirm this hypothesis. In the model of ME, for example, the hydrogen atoms on the  $\gamma$ -carbon atom make firm contact with either oxygen atom (these being equivalent in the anion), while those on the  $\beta$ -carbon atom, although they make contact, are constrained to do so at an unfavorable angle.

On the other hand, it is mechanically possible to show, using the models, that unstrained puckered rings which are composed of chains more than six members long can be formed in acids like 2-bromohexoic (BH). However, the data indicate no extra stability for such structures; they are not anomalous in behavior. This apparent difficulty can be resolved by reference to the concept of an  $\alpha$ -lactone structure in the anion, as previously discussed. This structure constrains the  $\alpha$ -carbon atom, the carbonyl carbon atom, and the carbonyl oxygen atoms to lie in a plane. Under that constraint manipulation of the models demonstrates that the only C-H-O bond now possible is that involving the  $\gamma$ -carbon atom. With this assumption, the possibility of forming rings with a number of members other than six becomes remote.



There exists, of course, the converse possibility, namely, that the six-member ring augments the stability of the  $\alpha$ -lactone structure. This would be a desirable interpretation because one would expect the resistance to reduction to be related to the stability of the  $\alpha$ -lactone intermediate, which exists only near the electrode, and not to that of the ring, which, after all, might exist in the bulk of the solution as well as near the electrode.

In the data on the straight acids (1), the increment of potential associated with the anomaly cited (EH) is about 0.05 volts, corresponding to an energy increment for a two-electron process of 2.3 kcal./mole. Comparing this with the commonly accepted value of 5 kcal./mole for many hydrogen bonds, the value of 2.3 kcal./mole is of reasonable order of magnitude for a relatively weak manifestation. It is difficult to establish from the present data the magnitude of an analogous increment because of the absence of data on the longer chain side. However, some conclusions can be drawn. For example, the data show that EE must have a larger increment than either of its neighbors. (Fig. 1). This acid, as can be demonstrated with the Fisher-Hirschfelder-Taylor models, can so dispose itself that the two possibilities for  $-C-H-O$  bonds can be simultaneously realized, thus accounting for the increased stability.

Experimental anomalies involving six-membered chains have been reported. Newman (23) observed such an effect in the acid-catalyzed esterification of a large number of acids, and devised the concept of 6-member in elucidating a rule of thumb for predicting such anomalous behavior. However, the effect described by Newman differs from that encountered in the present work, in that once the possibility of achieving a six-membered ring has developed, subsequent increase in complexity of the terminal group has no influence.

On the other hand, Berlimer (24, 25), Dippy (26) and Evans (27, 28) have described anomalous behavior involving six-member chains, in which the

anomalies represent departure of one particular member of a series from a trend which continues in the series members on either side of the anomalous compound. The work of Dippy is of particular interest because of the close association of the compounds studied with those of the present work; he presents values of ionization constants for saturated straight chain aliphatic acids out to octanoic, and for certain of their branched chain isomers. There is a consistent decrease in  $K_1$  among the straight chain acids except for the striking anomaly of n-butyric acid, whose  $K_1$  is greatly in excess of the values for its neighbors in the series. In the branched series, diethylacetic acid and ethylmethylacetic acid are similarly anomalous. These are the parent acids of the very compounds found to show anomalies in the present work.

The authors cited have suggested formation of a cyclic six-member structure whose angles conform more closely than any other ring structure to the normal tetrahedral bond angle for carbon. The stabilization of this structure is supposed to be effected by a loose chemical connection which is discussed in terms of hydrogen bonding (Dippy), hyperconjugation (Berliner) or resonance (Evans). Hunter (29) in a review on hydrogen bonding states that C-H-O bonds are very weak, and are probably manifested only under some directing influence; such bonds are very difficult to detect. Nevertheless, even such a weak influence might exert sufficient stabilization on the structure to produce the effects observed.

If the energies of the various configurations possible in the  $\alpha$ -bromo aliphatic acids could be estimated, the problem of ring formation might be attacked by statistical mechanics. Energies associated with the strain produced by various configurations, and energies associated with bond rotation would have to be estimated, as well as the energies resulting from approach of the terminal atoms. From these, a partition function could be constructed. It would then be necessary to compute

the populations of those configurations approximating to a six-membered ring, five-membered ring, unclosed U, straight chain, etc., for several of the acids, to find out if there is any exceptional stabilization associated with the six-membered ring configuration. Work of this type has been carried out for hydrocarbons (30).

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#### Bibliography

1. Rosenthal, I., Allbright, C. H., and Elving, P. J., J. Electrochem. Soc., 99, 227 (1952).
2. Elving, P. J., Rosenthal, I., and Kramer, M. K., J. Am. Chem. Soc., 73, 1717 (1951).
3. Rosenthal, I. and Elving, P. J., J. Am. Chem. Soc., 73, 1880 (1951).
4. Elving, P. J. and Tang, C.-S., J. Am. Chem. Soc., 74, 6109 (1952).
5. Rosenthal, I., Tang, C.-S., and Elving, P. J., J. Am. Chem. Soc., 74, 6112 (1952).
6. Elving, P. J., Komyathy, J. C., Van Atta, R. E., Tang, C.-S., and Rosenthal, I., Anal. Chem., 23, 1218 (1951).
7. Brdicka, R. and Wiesner, K., Collection Czechoslov. Chem. Commun., 12, 138 (1947).
8. Koutecky, J. and Brdicka, R., Collection Czechoslov. Chem. Commun., 12, 337 (1947).
9. Saito, E., Bull. soc. chim. France, 1951, 957.
10. Kolthoff, I. M. and Lingane, J. J., "Polarography," 2nd ed., Vol. I, Interscience Publishers, New York, 1952.
11. Alexander, E. R., "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, 1950.
12. Hammett, L. P., "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940.
13. Grunwald, E. and Winstein, S., J. Am. Chem. Soc., 70, 841 (1948).
14. Kemball, C., Proc. Roy. Soc. (London), A190, 117 (1947).

15. Elving, P. J. and Westover, L. C., unpublished work.
16. Brown, H. C., Bartholomay, H., and Taylor, M. D., J. Am. Chem. Soc., 66, 435 (1944).
17. Brown, H. C. and Fletcher, R. S., J. Am. Chem. Soc., 71, 1845 (1949).
18. Taft, R. W., Jr., Office of Naval Research, Technical Report on Project NRO55-328, April, 1953.
19. Haggarty, C. J., Trans. Am. Electrochem. Soc. 56, 421 (1929).
20. Wheland, G. W., "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, 1949.
21. Thiessen, G. W., Trans. Illinois State Acad. Sci., 43, 77 (1950).
22. Coulson, C. A., Discussions Faraday Soc., No. 2, p. 11 (1947).
23. Newman, M. S., J. Am. Chem. Soc., 72, 4783 (1946).
24. Berliner, E. and Berliner, F., J. Am. Chem. Soc., 71, 1195, (1949).
25. Berliner, E. and Berliner, F., J. Am. Chem. Soc., 72, 222 (1950).
26. Dippy, J., Chem. Revs., 25, 189 (1939).
27. Evans, D., J. Chem. Soc., 1936, 785.
28. Evans, D. and Gordon, J., J. Chem. Soc., 1938, 1434.
29. Hunter, L., Ann. Repts. on Progress Chem. (Chem. Soc. London), 43, 141 (1946).
30. Taylor, W., J. Chem. Phys., 16, 257 (1948).

Table I. Polarographic data for 2-bromo-2-methylpropionic acid (MM)

Except as noted, temperature is 0°C., and mercury head is 50 cm. Diffusion coefficient, calculated from the Stokes-Einstein equation, is  $2.02 \times 10^{-6}$ .  $n$ -value, calculated from Ilkovic equation, is 2.

pH	Acid Concn. mM	$-E_1$ $\frac{1}{2}$ v.	$\alpha$	$i_d$ $\mu a.$	I	Notes
1.07	0.521	0.279	0.65	1.48	2.05	a
	0.521	0.287	0.60	1.82	2.06	a,b (R = 1.23)
	0.260	0.287	0.58	0.765	2.12	c
	0.260	0.283	0.62	0.945	2.10	c,b (R = 1.24)
	0.521	0.213	0.60	2.59	3.40	d ( $C_1 = +2\%/deg.$ ) ( $C_e = +1.13\%/deg.$ )
1.80	0.521	0.287	0.60	1.46	2.02	a
	0.260	0.275	0.60	0.675	2.12	c
4.01	0.521	0.473	0.31	1.08	1.50	
4.80	0.521	0.577	0.27	1.26	1.72	
5.60	0.521	0.795	0.21	1.31	1.81	
7.79	0.521	1.059	0.34	1.35	1.89	
8.87	0.521	1.066	0.33	1.26	1.75	
	0.521	1.092	0.37	1.74	1.95	b (R = 1.38)
	0.521	1.022	0.34	2.22	2.93	d,e ( $C_1 = +2\%/deg.$ ) ( $C_e = +0.25\%/deg.$ )
	0.589	1.059	0.33	1.38	1.70	
	0.589	1.090	0.30	1.86	1.85	b (R = 1.34)

a - Maximum present.

b - Mercury head = 75 cm. R = diffusion current ratio for mercury head (75 cm.:50 cm.); for diffusion control, expected value is 1.23.

c - Concentration decreased to eliminate maximum.

d - Run at 25°C.  $C_1$  is temperature coefficient of I; expected value for diffusion control is about +2%/degree.  $C_e$  is the temperature coefficient of  $E_1$ .

e - Diffusion current corrected for hydrolysis.

Table II. Polarographic data for 2-bromo-2-methylbutyric acid (ME)

Except as noted, the temperature was 0°C. and the mercury head was 50 cm.

Diffusion coefficient is  $1.97 \times 10^{-5}$ .  $n$ -value (Ilkovic) = 2.

pH	Acid Concn. mM	$-E_{\frac{1}{2}}$ v.	$\alpha$	$i_d$ $\mu a.$	I	Notes
1.07	0.508	0.252	0.60	1.35	1.89	f
	0.102	0.264	0.68	0.324	2.28	c
1.80	0.508	0.256	0.67	1.29	1.81	f
	0.508	0.254	0.72	1.36	1.91	g
	0.465	0.246	0.62	1.64*	1.74	f, b (R = 1.21)
	0.465	0.260	0.65	1.20	1.81	f
	0.093	0.250	0.68	0.273	2.12	c
	0.534	0.268	0.59	1.62	2.22	f, h
	0.465	0.184	0.66	2.10	3.08	d ( $C_1$ = +2.4%/deg.) ( $C_e$ = +1.4%/deg.)
4.01	0.513	0.395	0.31	0.99	1.37	
	0.513	0.378	0.31	0.96	1.33	h
4.80	0.508	0.490	0.27	1.12	1.60	
5.60	0.508	0.694	0.23	1.04	1.47	
7.79	0.508	1.028	0.26	1.15	1.65	
	0.534	0.949	0.28	1.08	1.46	h
	0.465	1.005	0.31	1.59	2.40	d ( $C_1$ = 1.5%/deg.) ( $C_e$ < +0.25%/deg.)
8.87	0.596	1.028	0.26	1.41	1.72	
	0.596	1.077	0.28	1.77	1.74	b (R = 1.25)

f - Gelatine concentration approximately 0.02%.

g - Gelatine concentration approximately 0.01%.

h - Alcohol concentration 3.8% by volume. Ionic strength 0.45.

\*This current has been corrected to permit comparison with preceding values obtained at a higher concentration.

Table III. Polarographic data for 2-bromo-2-ethylbutyric acid (EE)

Except as noted, the temperature was 0°C. and the mercury height was 50 cm. Diffusion coefficient is  $1.92 \times 10^{-6}$ . Ilkovic  $n$ -value is 2.

pH	Acid Concn.  mM	$-E_{\frac{1}{2}}$  v.	$\alpha$	$i_d$  $\mu a.$	I	Notes
1.07	0.72	0.224 0.182	0.61 0.67	1.64 2.64	1.52 2.52	d ( $C_1 = +1.75\%/deg.$ ) ( $C_e = +0.75\%/deg.$ )
1.80		0.216 0.222	0.70 0.73	1.74 2.22	1.73 1.76	b ( $R = 1.27$ )
4.01		0.385	0.30	1.26	1.25	
4.80		0.477	0.28	1.23	1.22	
5.60		0.711	0.23	1.38	1.37	
7.79		1.095	0.22	1.46	1.46	
8.87		1.065 1.090	0.29 0.26	1.35 1.68	1.37 1.38	1 b ( $R = 1.25$ )

1 - No temperature coefficient of I could be determined at this pH because of the extreme rapidity of hydrolysis at 25°C.

Table IV. Polarographic data for 2-bromo-2-ethylhexoic acid (BE)

Except as noted the temperature was 0°C. and the mercury height was 50 cm.

pH	Acid Concn.	$-E_{\frac{1}{2}}$	$\alpha$	$i_d$	I	Notes
	mM	v.		$\mu a.$		
1.07	0.494	0.142	0.7	1.17	1.68	b (R = 1.28)
	0.494	0.154	0.6	1.50	1.47	
1.41	0.221	0.163	0.9	0.59	1.9	
1.80	0.221	0.158	0.9	0.60	1.9	
	0.494	0.133	0.7	1.10	1.55	
5.60	0.494	0.452	0.4	0.90	1.3	
8.20	0.494	0.823	0.2	0.87	1.2	b (R = 1.28)
	0.494	0.832	0.4	1.11	1.26	
8.60	0.522	0.791	0.5	0.93	1.2	a
	0.266	0.771	0.4	0.49	1.3	
9.00	0.494	0.795	0.5	1.02	1.5	
	0.247	0.780	0.4	0.47	1.4	



Table V. Polarographic data for the esters of the 2-bromo acids

Except as noted, the temperature was 0°C. and the mercury height was 50 cm.

Ester	pH	Ester Concn.	$-E_{\frac{1}{2}}$	$\alpha$	$i_d$	I	Notes
		mm	v.		$\mu a.$		
EtMH	1.07	0.108	0.348	0.8	0.276	1.82	
	1.41	0.169	0.353	0.8	0.448	1.85	
	8.60	0.169	0.368	0.6	0.420	1.70	
EtEH	1.07	0.112	0.336	0.8	0.294	1.83	
	1.41	0.156	0.335	0.8	0.368	1.63	
	8.60	0.156	0.340	0.5	0.420	1.85	
EtMM	1.41	0.546	0.243	0.8	1.05	1.34	
	9.00	0.109	0.268	1.1	0.228	1.46	j
	9.00	0.109	0.269	1.1	0.216	1.39	j
	9.00	0.109	0.268	1.2	0.222	1.43	j
EtEE	1.41	0.509	0.212	0.8	1.08	1.48	
	1.41	0.102	0.205	0.6	0.300	2.05	k
EtBE	1.41	0.116	0.143	0.6	0.246	1.48	

j - Maxima present even at this low concentration.

Distortion of wave makes these data less accurate.

k - The current values here are inexplicably high.

Table VI. Polarographic data for bromoacetic acid (HH), 2-bromopropionic acid (MH) and 2-bromobutyric acid (EH).

The temperature for all these runs was 0°C., and the mercury height was 50 cm. Diffusion coefficients are  $2.15 \times 10^{-6}$ ,  $2.08 \times 10^{-6}$  and  $2.02 \times 10^{-6}$  for HH, MH and EH respectively. Ilkovic  $n$ -value is 2 in all cases.

Acid	pH	Acid Concn. mM	$-E_{\frac{1}{2}}$ v.	$\alpha$	$i_d$ $\mu a.$	I	Notes
HH	1.07	0.610	0.673	0.47	1.98	2.32	f
	1.80		0.673	0.50	1.88	2.20	f
	8.20		1.235	0.40	1.82	2.18	
	8.87		1.229	0.40	1.80	2.16	
	1.07		0.516	0.38	1.98	2.08	f
	1.80		0.557	0.39	1.88	1.98	f, l
MH	8.20	0.676	1.195	0.42	2.04	2.20	
	8.87		1.196	0.49	1.86	1.99	
	1.07		0.473	0.43	1.47	1.85	f
	1.80		0.498	0.41	1.53	1.93	f, l
	8.20		1.216	0.51	1.56	2.01	
	8.87		1.217	0.46	1.41	1.80	
EH	1.07	0.591	0.473	0.43	1.47	1.85	f
	1.80		0.498	0.41	1.53	1.93	f, l
	8.20		1.216	0.51	1.56	2.01	
	8.87		1.217	0.46	1.41	1.80	
	1.07		0.473	0.43	1.47	1.85	f
	1.80		0.498	0.41	1.53	1.93	f, l

l - This  $E_{\frac{1}{2}}$  value is larger than the preceding probably because it falls on the rising portion of the  $E_{\frac{1}{2}}$  vs. pH curve.

Table VII. Comparison of the half-wave potentials  
of the acids studied.

Temperature = 0°C.			Height of mercury = 50 cm.				
pH	HH	NH	EH	MM	ME	EE	BE
1.1	0.67	0.52	0.47	0.29	0.25	0.22	0.14
1.4	--	--	--	--	--	--	0.15
1.8	0.67	0.56	0.50	0.28	0.26	0.22	0.16
4.0	--	--	--	0.47	0.40	0.39	--
4.8	--	--	--	0.58	0.49	0.48	--
5.6	--	--	--	0.80	0.69	0.71	0.45
7.8	--	--	--	1.06	1.03	1.10	--
8.2	1.24	1.20	1.22	--	--	--	0.82
8.6	--	--	--	--	--	--	0.79
8.9	1.23	1.20	1.22	1.06	1.02	1.07	--
9.0	--	--	--	--	--	--	0.80

The values listed in this table are those considered  
by the authors as most reliable for each pH.

Fig. 1. Relation of  $E_1$  to chain length of the acid for alpha bromo acids and their ethyl esters. Solid lines: acids. Dotted lines: esters. Dashed lines: data for acids in reference 1.

